PATENT SPECIFICATION

NO DRAWINGS

827,043

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COMPLETE SPECIFICATION

Improvements in and relating to Bonded Molecular Sieves

We, UNION CARBIDE CORPORATION, of 30, East 42nd Street, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (assignee of WILLIAM JAMES MITCHELL and WARD FREDERICK MOORE), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to adsorbents of the molecular sieve type and more particularly to bonded zeolitic molecular sieves of the type described in our previous application No. 20146/56 (Serial No. 825,379) to which this is a patent of addition.

The zeolitic molecular sieves are natural or synthetic hydrated metal aluminium silicates having a three dimensional crystalline structure with the general formula

$$\frac{M_2O : Al_2O_3 : X\ SiO_2 : YH_2O}{n}$$

where M represents a metal and n its valence. When the water of hydration is removed as by heating the zeolite, a crystalline structure is left behind interlaced with channels of molecular dimensions offering very high surface area for the adsorption of foreign molecules. Adsorption is limited, however, to molecules having a size and shape such as permits entrance through the pores or openings of the channels into the inner sorption area. Other molecules are excluded. In this respect molecular sieves differ from the common adsorbents such as charcoal and silica gel.

Some of the zeolitic molecular sieves employed for separating molecules on the basis of molecular size and shape are the naturally occurring chabazite and the synthetic zeolites A and X described in Specifications Nos. 777,232 and 777,233.

As explained in application No. 20146/56 (Serial No. 825,379), the difficulties in handling these zeolites arising from their extremely fine particle size can be obviated by agglomerating the zeolite powders with a binder in such a manner that the binder does not reduce the adsorptive capacity of the zeolite by blocking off the pores. This is effected by using as binder a clay mineral.

We have now found that zeolites bonded with attapulgite (attapulgus clay) into substantially spherical pellets are particularly valuable for use in service where a minimum of dusting is a prime criterion.

As little as 3 parts of attapulgus clay to 97 parts of zeolite adsorbent will make spheroidal pellets. As much as 95 parts attapulgus clay to 5 parts of zeolite adsorbent can be used without substantially harming the adsorbtive capacity of the molecular sieve other than by dilution. About 20 parts of clay to about 80 parts of zeolite is the preferred composition.

In preparing the spherical pellets of clay-bonded molecular sieve, clay, molecular sieve and water are blended by any means which insures thorough mixing. Water is present in an amount sufficient to attain a semi-plastic state.

In each of the following examples, after formation of the spheres they were air dried and fired.

Spheroidal pellets can be made in an intensive sigmablade mixer. Slightly helical blades rotate in opposite directions across a trough giving a kneading, tearing, stretching and folding treatment to the material being mixed. The blend is placed in the mixer and water is added. After mixing for several hours, spheroidal pellets form.

Fifteen pounds of sodium zeolite A containing 25% water (dry basis); 2.62 pounds attapulgite (average particle size 0.077 microns); and 0.43 pounds kaolin clay were blended together in an intensive sigma-blade mixer. About five pounds of water were added and the batch mixed for three and one-half hours. Fifteen-hundredths pounds of sterotex (stearic acid) were added and after 75 minutes addi-

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tional mixing time crude spheroidal pellets were formed $\frac{1}{16}$ inch to $\frac{1}{8}$ inch diameter. These pellets were air dried at 90°C. for two hours and then fired in a rotary kiln for 16 minutes at 650°C. The pellets were subjected to the jet attrition test and suffered a 23% loss.

Spheroidal pellets can also be formed in a muller-mixer by adding water to the blend either before or after it is placed in the mixer. The batch is then mulled for about an hour. At this point mulling stops and while the mixing goes on, the batch is dried up by adding more blend or directing a flow of air on the batch. Another hour of mixing will produce pellets.

A blend containing 61 pounds of sodium zeolite A (21 wt—% H_2O, dry basis) and 12 pounds attapulgite (particle size 0.077 microns) was prepared in a powder blender by mixing for 30 minutes. Thirty pounds of this blend were charged into a muller-mixer with 9.9 pounds of water. After 95 minutes of mixing, spheres averaging $\frac{1}{4}$ inch diameter were formed. The Muller wheel was braked to prevent rotation. An unmeasured amount of the remaining dry blend was added to the mix during added mixing and the size of the sphere was reduced to about $\frac{1}{8}$ inch diameter. The pellets were air dried at 90°C. for two hours, fired at 650°C. for 16 minutes in a rotary kiln, and subjected to the jet attrition test. The loss was about 3.2 per cent.

Spheroidal pellets can be made by mulling blended powders of molecular sieve and attapulgus clay in a muller-mixer and charging the wet mix into a tumbling drum. Sufficient water is added in the muller-mixing step to make the batch plastic. The batch is then screened to remove agglomerates and the wet mix placed in the drum. The drum is then rotated at a speed that will bring the water to the surface of these finite particles; the speed is subsequently reduced slightly and the tumbling mass dried slightly with a blast of air. Spheroidal pellets are then formed by tumbling.

Forty-five pounds of sodium zeolite A and $9\frac{1}{2}$ pounds of attapulgus clay were blended in a dry powder blender. The blended powders were transferred to a muller-mixer and 8000 cc. water added. After mulling for about 20 minutes, $3\frac{1}{2}$ pounds of the wet batch were transferred to the inclined drum. These wet particles were tumbled in the drum containing small flights at about 30 r.p.m. for 20 minutes. The material compacted and formed balls $\frac{1}{16}$ of an inch to $\frac{1}{8}$ inch in diameter. After tumbling for another $\frac{1}{2}$ hour, the drum rotation was decreased to about 14 r.p.m. and the batch dried up in a blast of air. They were removed from the drum and air dried at 90°C. for 2 hours. The pellets were subsequently fired for 16 minutes in a rotary kiln at a hearth temperature of 650°C. and an air purge of 12 cubic feet per hour per pound of product per hour.

In the following tables, several tests were employed to show the properties of the spheroidal clay-bonded molecular sieves. They are described in detail below.

Air Jet Attrition Test:

The apparatus used for this test is an inverted conical flask with a hole in the bottom, fitted with a screen. The pellets are placed in the flask and air blown through. The pellets strike each other and the side of the flask in this blast of air and dust passes through the screen. Thirty grams of pellets are subjected to the air blast for 30 minutes. The screen used varied with the size of the pellet being tested. The Jet Attrition Index, used to provide a comparative evaluation value in this test method, is the percent of material larger than 10 mesh at the end of the test when pellets of 0.32 cm. size are evaluated. In the case of pellets of smaller starting size, the criterion is the percent of material larger than 14 mesh.

Ball Mill Hardness Test:

The apparatus used in this test consists of a jar with a steel liner. Inside the jar are placed seven steel balls, $\frac{1}{2}$ inch in diameter. The pellets are placed in the jar, tumbled for 15 minutes, screened, and the per cent survival measured. The Ball Mill Index is calculated in the same manner as the Jet Attrition Index.

Wet Attrition Test:

In this test, 100 cc. (unsettled) zeolite pellets are placed in a 4 oz. wide mouth jar ($1\frac{7}{8}$" inside diameter x $2\frac{5}{8}$" high). Fifty cc. of trichloroethylene are added, the jar sealed, and placed on a vertical pulsating mechanism having a vertical stroke of $1\frac{1}{8}$ inches and a frequency of 330 cycles per minute. Pulsation goes on for 450,000 cycles. The jar is removed and the dust is washed from the pellets using trichloroethylene and filtered with a screen U.S. sieve size 100 mesh. Trichloroethylene is then evaporated and the per cent loss calculated. The Wet Attrition Index is the percent of material smaller than 100 mesh at the end of the test.

TABLE I

STRENGTH OF CLAY-BONDED SODIUM ZEOLITE A PELLETS

Binder and Pellet Shape	Jet Attrition Index	Ball Mill Index	Wet Attrition Index
Kaolin —0.32 cm. cylinder	78.4	47.1	10.0
Kaolin —0.16 cm. cylinder	52.2	29.8	5.4
Attapulgite —0.32 cm. sphere	96.0	39.9	4.7
Attapulgite —0.16 cm. sphere	86.3	28.3	1.4
Kaolin —0.32 cm. sphere	0	5.9	—

These data show that while kaolin-bonded zeolites in cylindrical pellet shape are fairly resistant to attrition, the spheres made using attapulgite are markedly superior. It should be noted that the kaolin-bonded pellets were made by an extrusion process and the attapulgite-bonded pellets were prepared in a Muller-mixer. The data on kaolin-bonded spherical pellets show that kaolin is inferior as a bonding agent for pellets of this shape.

TABLE II

STRENGTH OF CLAY-BONDED CALCIUM A AND SODIUM X PELLETS

Binder and Pellet Shape	Jet Attrition Index	Ball Mill Index	Wet Attrition Index
Calcium Zeolite A			
Kaolin — 0.32 cm. cylinder	40.8	10.0	13.0
Attapulgite — 0.32 cm. sphere	92.2	12.4	8.3
Sodium Zeolite X			
Kaolin 0.32 cm. cylinder	2.7	11.5	16.5
Attapulgite 0.32 cm. sphere	69.5	9.8	10.0

These data show that the relative merits of attapulgite-bonding and kaolin-bonding are unchanged by changes in the zeolite being bonded. As was shown in application No. 20146/56, the parent case, bonding with clays does not affect the adsorptive capacity of the molecular sieves. For example, if 20% of the bonded product is non-adsorptive binder, the adsorptive capacity of the bonded product should be 80% of that of an equal weight of unbonded zeolite. This was shown to be generally true in the parent case; the data in Table III demonstrates that it is also true when attapulgite is used as binder.

TABLE III

EQUILIBRIUM ADSORPTION DATA FOR UNBONDED ZEOLITES AND ZEOLITES BONDED WITH 20% ATTAPULGITE CLAY

Zeolite	*Wt. % CO_2 Adsorbed at 250 mm. Hg. and 25°C.*	
	Bonded	Unbonded
Sodium A	14.5	17.4
Calcium A	17.5	22.2
Sodium X	18.4	22.0

WHAT WE CLAIM IS:—

1. An agglomerate comprising a zeolitic molecular sieve and a clay binder characterized in that the clay is attapulgite.

2. An agglomerate according to claim 1 which is formed into substantially spherical shape.

3. An agglomerate according to claims 1 or 2 in which the clay comprises between 1% and 40% by weight of the agglomerate.

4. An agglomerative according to claims 1, 2, or 3 in which the molecular sieve is a natural zeolite.

5. A process for producing the agglomerate of claims 1, 2, 3, or 4 comprising blending together water, a zeolitic molecular sieve, and attapulgus clay; compacting the blended material into pellets having a substantially spherical shape; drying the spherical pellets, and baking them at a temperature above 400°C. but below the temperature at which the structure of the molecular sieve is destroyed.

6. The process of claim 5 in which the baking temperature is from 425°C. to 520°C.

7. The process for preparing agglomerates and products thereof described and claimed herein.

W. P. THOMPSON & CO.,
12 Church Street, Liverpool, 1,
Chartered Patent Agents.

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